

**STUDIES ON SHRINKAGE PHENOMENON Pt. XIII:
AREA SHRINKAGE PROPERTIES OF LEATHER**

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Area shrinkage values of formaldehyde, fish oil, wattle and chrome leathers in water showed that fish oil tanned leathers shrink to a minimum extent and fish oil and formaldehyde tanned leathers recover to a considerable extent. The minimum area shrinkage of fish oil tanned leather may be mainly due to the incipient shrinkage taking place during the processing. The large area shrinkage of chrome leather, despite the fact that the skins are affected by incipient loss in area due to pickling confirmed that the nature of tannage and crosslinks have their effect on the shrinkage properties of leathers. Area recovery of chrome leather was poor but that of formaldehyde leather was considerable even though, in both the cases, forces of covalent type are involved. The difference in the recovery behaviour of the two may be due to finer differences in the linkages. The vegetable tanned leather exhibited poor recovery because of the weakness of the crosslinks involved in the tannage such as hydrogen bonds. That covalent links are not involved in vegetable tannage was proved by recent work.¹ It is established that the process liquor can be used as heating medium for measuring T_s and area shrinkage properties of wattle, formaldehyde and chrome leather. T_s and area shrinkage properties of these leathers in water and process liquor are the same.

The influence of various pretanning chemical treatments on T_s , area and apparent volume shrinkage and recovery characteristics of skins and collagen fibres were published²⁻⁶ recently and it was concluded that the use of process liquor as heating medium would give meaningful information on shrinkage properties of skin and collagen fibres subjected to pretanning chemical treatments as the use of process liquor as heating medium eliminates the influence of diffusion; the influence of diffusion materially altered the shrinkage characteristics in water of limed and pickled specimens. A study in the same direction may be extended to leathers. Some amount of work was done in this field earlier, but the earlier work was done under different experimental conditions.⁷ This is dealt with at some length at the appropriate place in this paper. In the present work, area shrinkage characteristics of wet non-dried leather, obtained by tanning the skins with four typical tanning agents viz., formalin,

wattle, sardine fish oil and basic chromium sulphate representing commonly used aldehyde, vegetable (condensed), fish oil and mineral tanning agents were studied. For statistical evaluation of area shrinkage and recovery values (AS and AR) 48 samples of a specific type of leather were tested in water and compared wherever necessary with the shrinkage characteristics in water of delimed skin samples cut out previously at the location adjacent to that of the leather specimen, as the adjacent sample of hide or skin showed less variation than any other pair. Samples of skins cut out from the position marked as 4 in Fig. 1 of the previous publication² were used for studying the shrinkage behaviour in water of tanned specimen and compared with that of delimed samples cut out from the adjacent position 3 in water. For knowing the effects of diffusion of chemicals incorporated into skins for making leather into water—the commonly used heating medium for shrinkage, the leather samples cut out from the position 5 adjacent to 4 were used for studying the shrinkage behaviour of leather sample 5 was tested in respective process liquor and compared with that of adjacent piece (Sample 4) tested in water.

Experimental

Determination of shrinkage values:

T_s of vegetable, formaldehyde and fish oil tanned leathers in water or process liquor were determined in a Theis shrinkage meter wherein the sample is subjected to tension of 50 g. balancing

load used to keep the sample straight. This equipment and procedure were used in this work as this work is a continuation of the work on shrinkage properties of skins subjected to pretanning treatments wherein the Theis meter was used for measuring the shrinkage.²⁻⁴ T_s of chrome tanned leather, however, could not be determined in water or process liquor in Theis meter as its T_s is more than 100°C in water or process liquor. Hence, a pressure shrinkage vessel similar to the one developed by Fein *et al*¹⁸ was used for measuring the T_s of chrome leather in water or process liquor. But, in this apparatus, samples were not subjected to tension as in the Theis meter; hence a correction factor is necessary for the T_s value in water or process liquor of chrome leather determined in a pressure vessel. For this work, chrome leather was deliberately prepared so as to have a T_s less than 100°C and the T_s was determined in Theis meter in water or process liquor (adjusted to pH 3.9). Subsequently the T_s of an adjacent sample of the leather was determined in the pressure shrinkage vessel in water or process liquor as the case may be. The difference in T_s values obtained by these two techniques both in the case of water and process liquor medium was only 3°C, the value being higher when measured with Theis meter. Hence, 3°C is added to the T_s values of chrome leather in water or process liquor obtained in the pressure meter.

AS and AR characteristics of variously tanned leathers were studied by Nayudamma *et al*⁷ but those results do

not pertain to completely shrunk samples which is the case in the present series of experiments. As the samples are completely shrunk in the experiment, the shrinkage state value are not influenced by the "rate of transfer of heat". If the shrunk state measurements of dimensions are carried out at laboratory temperature, which was the experimental condition of Nayudamma *et al.*,⁷ the shrunk sample might recover as the result of cooling; for instance formaldehyde leather samples recover on cooling. To avoid this effect in the area shrinkage experiment, the leather samples shrunk completely in the free state by the procedure described in a previous paper, were placed in between two glass plates which in turn were placed over a micro hot plate, the temperature of which was maintained at about 5°C above the temperature at which shrinkage was known to take place and outlines of the samples were traced in that condition on a tracing paper for area shrinkage measurements of shrunk state. The two glass plates were also kept at a temperature about 5°C above the T_s of the sample being tested to prevent the cooling of the samples and the consequential recovery. From the area of sample before shrinkage, on complete shrinkage in the heating medium, on overnight recovery in the heating medium percentages AS and AR were calculated.

Tanning of skins:

This being the continuation of our earlier experiments on shrinkage behaviour of skins subjected to pretanning

treatments, skins of freshly slaughtered 1-year old male goat were used in this set of experiments and processed upto deliming by the procedure described earlier,² for use in formaldehyde, vegetable and chrome tanning treatment as such. Earlier researchers, however, used acetone dehydrated pelt. The necessity to adopt this method was dealt with in detail earlier.² In the case of fish oil, however, the pelt had to be acetone dehydrated as the delimed pelts prepared by the "common" procedure described earlier is less opened up and the fish oil did not penetrate "the less opened up grain" i.e. the skins whose grain layer was not removed. An attempt was made to subject the skins to the same amount of mechanical action for all tannages studied so that the effect of mechanical action is constant in all the cases. This was done by (a) subjecting skin for the same amount of drumming action in identical drums of same r.p.m. during various tannages and (b) using the same quantity of float while drumming. The details of tanning treatments are given below:

(a) Formaldehyde tanning:

Delimed goat skins (10 Nos.) are washed well to free them completely from ammonium sulphate—the chemical used for deliming since ammonium compounds form condensation products with formaldehyde. These pelts were treated with 3% formalin (40%) for 3 hours in a slow moving drum (10 rpm) maintaining a float of 100%. Then the pH of the bath, while drumming, was raised to 8.2 by soda ash for attaining

the maximum fixation of aldehyde. The total period of drumming was 6 hours.

(b) *Vegetable tanning:*

The delimed goat skins were treated with 10°Bk wattle liquor (1.2% tannin) for a period of 10 days in a pit maintaining a float of 600%, changing to fresh liquor of the same concentration after 5 days of tanning. The skins were frequently handled during tanning and on the last day (10th day of tanning) they were transferred into the slow moving drum of 10 r.p.m. and drummed for 6 hours in 100% float of the vegetable tan liquor of the pit.

(c) *Fish oil tannage:*

Ten delimed goat skins were acetone dehydrated by treating them with 50% aqueous acetone for 2 days followed by 100% acetone for 5 days and finally leaving them in 100% fresh acetone. They were taken out of the final acetone bath after two days. Fish oil emulsion was applied to both the surfaces of the skins, the emulsion having been prepared by adding 5% water and 2% soda ash as 10% solution to fish oil and drummed intermittently in the 10 r.p.m. drum. At the end of each period of drumming, the skins were taken out and hoisted for half an hour for oxidation of the fish oil, before feeding the skins into the drum for intermittent drumming after applying the fish oil emulsion again on both the surfaces of skins. This was continued till 25% (on pelt weight) of fish oil was applied to the skins. The skins were then hung in a hot chamber maintained at 45–50°C and 70–75% R.H. for

one week. The skins tanned with fish oil in this manner were degreased by washing twice in a 2% lukewarm (45°C) solution of soda ash for two hours in a drum and then with 1½% soap + ½% soda ash solution for 1 hour. Finally, the skin were washed well with water. Here again, the total period of drumming in 10 r.p.m. drum for tanning and washing was 6 hours.

(d) *Chrome tannage:*

Delimed pelts were first pickled with 1½% sulphuric acid and 8% salt in 100% float and then tanned in a fresh bath of a commercial chrome extract containing 2.5% Cr_2O_3 on pelt weight and salt, 2% on pelt weight in the drum (10 r.p.m.) maintaining a float of 100% for 3 hours. During the chrome tanning, chrome was fed in three instalments, each having 30%, 30% and 60% basicity. Next day, the lot was neutralised to pH 5.0 by treating with ½–1% sodium bicarbonate (on pelt weight) in a float of 100% for 3 hours. T_s of these leathers is more than 100°C. By incorporating 0.75% Cr_2O_3 adopting the same procedure, leathers having T_s 100°C were obtained.

Results and discussion

It could be seen from the Table 1 that as expected, the maximum and minimum T_s values are respectively exhibited by chrome and fish oil tanned leathers while the T_s of vegetable and formaldehyde leathers are in between.

Since AS values of delimed skin samples used as control for variously tanned leathers are almost the same and

Table 1
SHRINKAGE TEMPERATURE AND AREA SHRINKAGE PROPERTIES OF LEATHER

Shrinkage value	Delimed skins (control)	Leather			
		Vegetable tanned	Fish oil tanned	Formaldehyde tanned	Chrome tanned
T_s , °C	61	87	60	89	106
Area shrinkage					
%	57 ± 7	78 ± 6			
	57 ± 7		52 ± 8		
	54 ± 7			68 ± 11	
	55 ± 7				70 ± 6
Area recovery					
%	13 ± 3	3			
	13 ± 3		54 ± 9		
	14 ± 3			34 ± 6	
	13 ± 4				5

since in all the tannages, the skins are subjected to the mechanical action to the same extent it could be said that the extent of shrinkage in area of vegetable chrome and formaldehyde tanned skin is high whereas that of fish oil tanned skin is very poor. During recovery, fish oil and formaldehyde tanned skins recover to an appreciable extent whereas the recovery of vegetable and chrome leathers is poor.

It should be noted, in this connection, that in fish oil and chrome tannages there is a reduction in area due to processing² and it is reasonable to expect this factor to exert its influence on AS values as in the case of values of pickled or limed skin samples of pretanning stage.² It was observed that loss in area on fish oil tanning of delimed skin was 23-26% and on chrome tanning was about 21-24%. Loss in area due to chrome

tanning is mainly due to the pickling and its effect (dehydration since loss in area on pickling is 10-16%) and a part of it may be due to chrome tanning. It may be mentioned that Okamura *et al*⁹ reported that the area of acetone dehydrated pelt is increased on chrome tanning but in the present experiment pelts used for chrome tanning are not acetone dehydrated ones. The loss in area on tanning with fish oil is probably due to the fact that during fish oil tannage along with the tanning with fish oil oxidation products, mostly aldehydes or expodies, denaturation due to the heat developed during oxidation may also take place, i.e. fish oil tannage is a shrunken tannage.

Okamura *et al*⁹ also reported that on tanning the acetone dehydrated pelt with vegetable tannins, the area is increased. It is again to be stressed that acetone de-

hydrated pelts are not used but only delimited pelts for vegetable tanning. It is quite possible that by loading the pelt with vegetable tanning materials to an extent more than that of the quantities used in the present experiment, there may be a reduction in area on tannage.

It is suggested that the incipient change in area during leather making is responsible for poor AS of fish oil. But this may not be the sole factor since shrinkage of tanned materials is influenced by other factors such as nature of crosslinks incorporated by tanning. Fairly appreciable AR values of fish oil and formaldehyde tanned skins are due to this. The fact that the nature of tannage is very important is demonstrated by the behaviour of chrome tanned specimens. AR value of chrome tanned specimens is very low as compared to that of fish oil tanned skin. In view of the fact that the incipient shrinkage of chrome tanned leather is not much less than that of fish oil tanned skin. AR value of chrome leather should have been close to that of fish oil tanned leathers, if incipient shrinkage is the only factor influencing the dimensional shrinkage, but this is not the case. Poor AR of chrome tanned leathers in contrast to the good recovery of formaldehyde or fish oil tanned materials also shows that another factor, namely hydrophobic character of the particular tannage and the nature of covalent linkages incorporated are also to be considered.

If AS values of leathers studied in the present work are compared to those published earlier,⁷ it is obvious that the

different experimental conditions referred to manifested in different AS values. AS values of all the leathers as reported earlier⁷ were poor which might be due to "partial shrinkage condition" of the experiment i.e. the samples meant for AS were not completely shrunk. This partial shrinkage has its own projection on the AR values of the samples.

The T_g characteristics of various types of leather and the factors that influences it are too well known to be discussed. It is obvious that though both chrome and formaldehyde incorporate covalent type crosslinks in the skins, their T_g need not be the same; nature and number of crosslinks coupled with hydrophobic characteristics of chrome are responsible for greater rise in T_g of chrome leathers. Formaldehyde alone cannot raise the T_g of skins to a value greater than 90°C as chrome. If vegetable tannins are to fix by covalent linkages to collagen at least to some extent as thought¹⁰ of by a school of thought, then vegetable tanned skins should have exhibited good recovery or it should possess hydrophobic characteristics as chrome but this was not so. This indicates that vegetable tannins may not fix covalently to collagen. This view is confirmed in a recent publication¹ on the mechanism of vegetable tannage. Since no significant difference was observed in the T_g and area shrinkage values in water and respective process liquors of vegetable, chrome and formaldehyde leathers, the results are not given. Fish oil used for processing of skins gets thickened due to oxidation and could not be used in the study of shrinkage of fish oil tanned leather with refer-

ence to the use of process liquor as the heating medium. The absence of change in T_g and AS characteristics of wattle, formaldehyde and chrome tanned leather does not mean that there is no physical or physico-chemical change taking place within the leather samples subjected to a shrinkage in water and in the respective process liquor e.g., if formaldehyde leather shrunk in the formaldehyde process liquor itself, there is a possibility of more formaldehyde getting fixed to the leathers as formaldehyde fixes more to the collagen at higher temperature.^{11,12} This and other factors in the other tannages studied, however, did not materially alter the shrinkage characteristics of leather on using the respective process liquor as test medium instead of water.

It is clear from the results that the process liquor can be used as heating medium for vegetable, chrome and formaldehyde leathers in area shrinkage studies. As it was reported earlier that use of process liquor results in the T_g and AS values free from the influence of diffusion of chemicals from the specimen into the heating medium, which possibility exists if water is used as the heating medium. It can be said that the use of process liquor as heating medium is beneficial in avoiding the diffusion effect.

Acknowledgement

This research was financed in part by the United States Department of Agriculture, Agricultural Research Service under PL-480.

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